Biomagnification of PCBs and 2,3,7,8-substituted polychlorinated dibenzo-p-dioxins and dibenzofurans in New Zealand's Hector's dolphin (*Cephalorhynchus hectori*).

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1) Introduction

Planar chlorinated hydrocarbons (PCHs) such as polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) and some polychlorinated biphenyl (PCB) congeners are ubiquitous contaminants in aquatic ecosystems. They have been detected in fresh water and marine organisms at high concentrations in the northern hemisphere. Concentrations in the marine environment in the southern hemisphere are considerably lower[1,2] and it is believed that atmospheric transport accounts for the bulk of these compounds found in the southern oceans[2]. While considerable data is available on such contaminants in marine mammals[3], studies of the origin and biomagnification of these contaminants are limited[4,5].

New Zealand's Hector's dolphin (*Cephalorhynchus hectori*)[6] has several advantages for the study of contaminant accumulation. It is a small dolphin which, although rare, strands relatively frequently on the New Zealand coast. This species also inhabits shallow (<20m) inshore waters within a limited home range (<30km). In addition, Hector's dolphin is a generalist feeder taking a wide range of food species[6]. This dolphin therefore offers a unique opportunity to examine local contaminant sources. Over the past several years, we have obtained contaminant data for Hector's dolphin[1,7,8] with many of the specimens being collected from the Banks Peninsula area, one of the species population centres. To expand this study and to assess the passage of PCDDs, PCDFs and PCBs through the food chain to the dolphins, we have collected sediment and fish samples from the same region.

2) Methods

All Hector's dolphin tissues were obtained from deceased stranded or accidentally killed animals. Dolphin blubber samples were collected from dolphins from several locations around the New Zealand coast including the west and east coasts of the South Island as well as the Banks Peninsula area. Blubber samples were stored frozen until analysis.

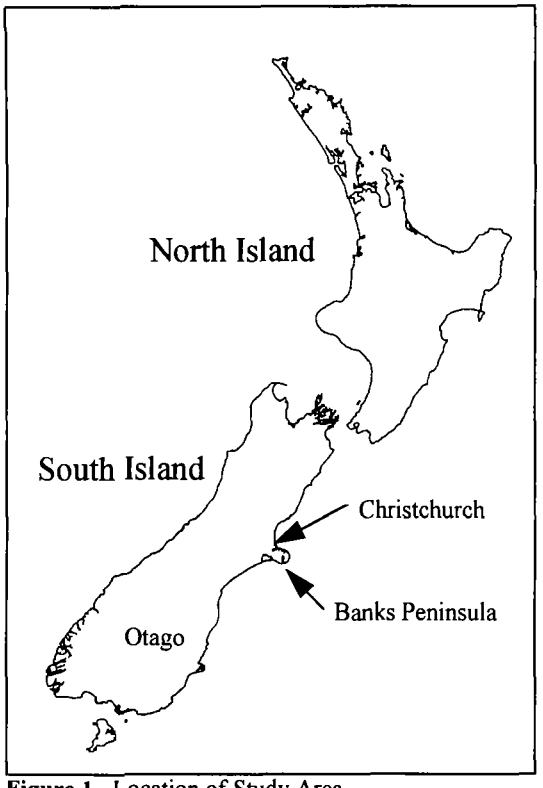

Figure 1. Location of Study Area.

The fish samples were collected by a commercial fishing vessel trawling off the north east coast of Banks Peninsula. Eight fish species were selected for analysis: skate (*Raja australis*); gurnard (*Chelidonichthys kumu*); dogfish (*Squalus acanthias*); pigfish (*Congiopodus leucopaecilus*); flounder (*Rhombosolea* spp.); common sole (*Peltorhamphus novaeseelandiae*); lemon sole (*Pelotretis flavilatus*); and cardinal fish (*Caelorinchus spp.*). The species selected reflect a wide range of feeding habits and trophic levels and are species which frequent the coastal waters inhabited by the dolphins. The fish were collected from the north east coast of the peninsula. For analysis, fish were ground whole in a commercial tissue grinder to provide composite samples. A 1kg aliquot of the homogenized composite was transferred to a solvent cleaned glass jar for storage at minus 20°C prior to analysis.

Marine sediments were collected from nine locations around Banks Peninsula. These included samples from the Avon/Heathcote Estuary in the city of Christchurch and from bays adjacent to the port of Lyttleton as well as isolated bays on the southern side of the peninsula. Sediment samples were collected by digging a 20cm cube of sediment from near the low water mark. The sediment was transferred to a cleaned plastic bin and homogenized thoroughly. A 1kg aliquot of the mixed sediment was transferred to a cleaned glass jar for transportation and storage. Sediments were stored at 4°C prior to analysis.

Methods for the analysis of PCDD, PCDF and PCB congeners in marine mammal tissues have been reported previously[1,7]. Briefly, after the addition of $^{13}C_{12}$ surrogate standards, samples were extracted with 2:1 acetone:hexane by homogenizing in the presence of anhydrous sodium sulphate. Extracts were concentrated and a small portion was removed for lipid determination. Extracts were purified by treatment with concentrated H_2SO_4 followed by chromatography using acid and base modified SiO_2, neutral Al_2O_3 and carbon dispersed on Celite. Coplanar PCBs were isolated using Florisil column chromatography. PCDDs, PCDFs and PCBs were determined by HRGC/HRMS on a VG 70 mass spectrometer using previously described methods[7].

All statistical analyses were performed using the SYSTAT© [9] statistical package. As the dolphin analyses have been conducted over a number of years, the range of contaminants measured has increased. For Principal Components Analysis (PCA) only variables for which data was available for all samples were used. For PCDD and PCDF congeners, all 2,3,7,8- substituted congeners were used

with the exception of 1,2,3,4,7,8-HxCDF and 1,2,3,4,7,8-HxCDD which were not resolved from the respective 1,2,3,6,7,8- isomers in early analyses. For PCBs, data for congeners 28+31, 52, 101, 99, 105, 118, 153, 138, 170, 180, 183, and 187 was available for all samples.

3) Results

PCDD, PCDF and PCB congeners were detected at quantifiable concentrations in all dolphin samples analysed. In contrast, PCDD and PCDF congeners were detected in only two of the sediment samples and in seven of the nine fish samples. PCBs were more commonly detected with congeners 153 and 138 being the predominant congeners found in six of the nine sediment samples and in all fish samples.

To assess variation in contaminant profiles PCA was performed after standardization of data to equalise weightings for all PCDD, PCDF and PCB variables (Figure 2). Little variation in congener profiles was observed in fish or sediment samples. This was illustrated by the tight clustering of these samples, compared with the variation observed in congener profiles from dolphin blubber (Figure 2). The exception to this was two sediment samples from the Avon/Heathcote Estuary. These two samples were the only sediment samples with significant levels of PCDD and PCDF congeners.

Due to the high proportion of 'non-detect' values for PCDD and PCDF congeners in the fish and sediment samples, PCA was also performed using only data for the most abundant PCB congeners which were detected in all samples (Figure 3). Limited variation in fish and sediment samples was also observed when PCA was conducted using this PCB data (Figure 3).

In both PCA analyses dolphin samples from geographically related regions cluster together. The cluster for the Canterbury region, north and south of Banks Peninsula, overlap with that from the opposite side, the western coast of the South Island. In contrast, a group of four dolphins from the Otago region, immediately south of the Canterbury region on the east coast, cluster well away from the Canterbury and West Coast clusters. A group of four open ocean cetaceans, three common dolphins and one minke whale were included in the PCA analysis for comparison with the Hector's dolphin samples. These specimens cluster away from the Hector's dolphin samples although the segregation is more apparent in the 'PCB only' analysis (Figure 3), presumably due to the previously demonstrated differences in PCB congener profiles in open ocean marine mammals[8].

2,3,7,8-TCDD Toxic Equivalents (TEQs) were calculated using the Toxic Equivalency Factors (TEF) values of Ahlborg *et al.* (1988)[10] for PCDD and PCDF congeners and the TEF values of Ahlborg *et al.* (1994)[11] for PCB congeners. PCB congeners analysed in the fish and sediment samples included some congeners with non-zero TEF values that had not been analysed in dolphin samples. However, the combined contribution of these congeners (114, 123, 156, 157, 167, and 189) was less than 16% of the total PCB TEQs. Therefore, omission of these congeners from dolphin TEQ calculations would not greatly alter the results.

TEQ concentrations were highest in Hector's dolphin blubber and lowest in fish samples (Table 1). Concentrations of all PCHs were generally lower in fish than in sediments. This phenomenon has been noted in previous biomagnification studies in aquatic ecosystems [12]. It is believed that this decrease in contaminant concentrations is due to the rate limiting nature of the release or uptake of contaminants from sediments.

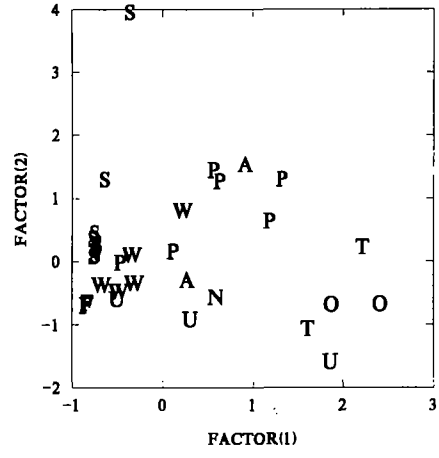

Figure 2. Principal Components Analysis using PCDD, PCDF and PCB congener data.

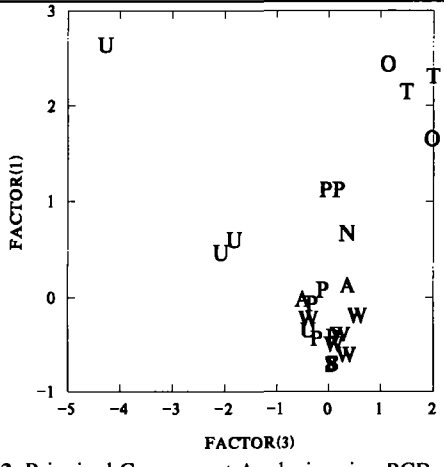

Figure 3. Principal Component Analysis using PCB data only.

Legend:
Markers on Figures 1 and 2 indicate sample type F = fish, S = sediment. Sample collection location for Hector's dolphin samples. W = west coast of the South Island; P = Pegasus Bay, north of Banks Peninsula; N = between Pegasus Bay and Banks Peninsula; A = Akaroa Harbour on Banks Peninsula; T = Timaru, 200km south of the Banks Peninsula area; O = Otago, an additional 100km south of Banks Peninsula; U=open ocean cetaceans, 3 common dolphins and one minke whale.

Table 1. Mean TEQ and PCB concentrations and Biomagnification Factors (BMFs) for contaminants in New Zealand marine sediments and biota.

	2,3,7,8 TCDD (pg/g)	OCDD (pg/g)	PCDD/F TEQ (pg/g)	ΣPCB (ng/g)	PCB TEQ (pg/g)	ΣTEQ (pg/g)	ΣTEQ/ ΣPCB
Hector's Dolphin	2.77	26.8	8.83	1770	72.3	81.1	0.05
Fish	0.03	0.13	0.1	1.42	0.31	0.41	0.29
Sediment	0.33	44.9	1.31	1.87	0.24	1.55	0.83
BMF(Dolphin/Fish)	8.4	0.6	6.8	948	300	52.4	
BMF(Fish/Sediment)	0.08	0.003	0.08	0.76	1.3	0.27	
BMF(Dolphin/Sediment)	102	209	89.8	1247	230	197	

4) Discussion

The higher concentration of contaminants in the dolphin samples is clear evidence of the biomagnification of these contaminants in this aquatic food chain. Biomagnification Factors (BMFs) from fish to dolphins were higher for PCBs than for PCDD and PCDF congeners. This can be attributed to the high number of non-detect values for PCDD and PCDF in the fish analysed.

While BMFs for the biomagnification of PCDD and PCDF congeners are within previously reported ranges, the BMF for the transfer of PCBs between the dolphins and fish (BMF=948) is higher than those previously reported for other open ocean[5] (BMF=54.4) or freshwater dolphin species[4] (BMF=22.7). This difference is largely due to lower concentrations of PCHs in food species in New Zealand compared with those found in these other studies. In contrast, PCH concentrations in the marine mammal samples from New Zealand are generally within one order of magnitude of concentrations found in similar species in the northern hemisphere. Similar observations have been made concerning the biomagnification of organochlorines in the New Zealand fur seal[13].

It therefore seems that a fugacity type model may be useful in explaining the accumulation of PCHs in marine mammals. This model suggests that all marine mammals are approaching a similar PCH concentration and that the key factor determining an individuals tissue PCH concentration is the kinetics of the uptake process. In areas with relatively low environmental PCH concentrations, such as New Zealand, the kinetics of uptake are relatively slow. Therefore, tissue PCH concentrations are lower than those reported in northern hemisphere marine mammals. This model explains why New Zealand marine mammals have similar organochlorine concentrations to northern hemisphere species while ambient environmental concentrations are usually several orders of magnitude lower.

5) Acknowledgments

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6) References

1. Hannah, D.J., Jones, P.D., Buckland, S.J., van Maanen, T., Leathem, S.V., van Helden, A., and Donoghue, M. (1993): Planar Chlorinated hydrocarbons in southern ocean marine mammals. *Organohalogen Compounds* 12 ISBN 3-85457-130-5: 333-335.
2. Iwata, H., Tanabe, S., Sakai, N., and Tatsukawa, R. (1993): Distribution of persistent organochlorines in the oceanic air and surface seawater and the role of ocean on their global transport and fate. *Environ. Sci. Technol.*, 27, 1080-1098.
3. Tanabe, S., Mori,T., Tatsukawa, R., and Miyazaki, N. (1983): Global pollution of marine mammals by PCBs, DDTs, and HCHs (BHCs), *Chemosphere*, 12, 1269-1275.
4. Kannan, K., Tanabe, S., Tatsukawa, R., and Sinha, R.K. Biodegradation capacity and residue pattern of organochlorines in Ganges river dolphins from India. *Toxicol. Environ. Chem.* 42:249-261, 1994.
5. Tanabe, S., Tanaka, H., and Tatsukawa, R. (1984): Polychlorobiphenyls, åDDT, and hexachlorocyclohexane isomers in the western north Pacific ecosystem. *Arch. Environ. Contam. Toxicol.* 13, 731-738.
6. Slooten, E., and Dawson, S.M. (1994): Hector's dolphin *Cephalorhynchus hectori* (van Beneden, 1881). *Handbook of Marine Mammals* 5:311-333, 1994.
7. Buckland, S.J., Hannah, D.J., Taucher, J.A., Slooten, E., and Dawson, S. (1990): Polychlorinated Dibenzo-p-dioxins and Dibenzofurans in New Zealand's Hector's Dolphin. *Chemosphere* 20, 1035-1042.
8. Jones, P.D., Hannah, D.J., Buckland, S.J., van Maanen, T., Leathem, S.V., Dawson, S., Slooten, E., van Helden, A., and Donoghue, M. (1996): Planar chlorinated hydrocarbons in New Zealand marine mammals. *International Whaling Commission Special Issue* (IN PRESS).
9. SYSTAT© for Windows, Version 5. Evanston IL: Systat, Inc., 1992. 264pp.
10. Ahlborg, U.G., Hakansson, H., Waern, F., and Hanberg, A. (1988): Nordisk dioxinriskbedoming. Rapport fran en nordisk expertgrupp. Norisk Ministerradet, Miljorорapport.
11. Ahlborg, U.G., Becking, G.C., Birnbaum, L.S., Brouwer, A., Derks,H.J.G.M., Feeley,M., Golor, G., Hanberg, A., Larsen, J.C., Liem, A.K.D., Safe, S.H., Schlatter, C., Waern, F., Younes, M., and Yrjänheikki, E. (1994): Toxic Equivalency factors for dioxin-like PCBs. Report on a WHO-ECEH and IPCS consultation, December 1993. *Chemosphere*, 28, 1049-1067.
12. Jones, P.D., Ankley, G.T., Best, D.A., Crawford, R., DeGalan, N., Giesy, J.P., Kubiak, T.J., Ludwig, J.P., Newsted, J.L., Tillitt, D.E., and Verbrugge, D.A. (1993): Biomagnification of bioassay derived 2,3,7,8-tetrachlorodibenzo-p-dioxin equivalents. *Chemosphere* 26:1203-1212.
13. Day, P.J. (1996): The bioaccumulation of persistent organochlorine contaminants in a New Zealand marine foodchain. MSc Thesis, Victoria University of Wellington, Wellington, New Zealand.